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Spectroscopy and Structure of Jet-Cooled α -Methylstyrene

by

V. H. Grassian, E.R. Bernstein, Henry V. Secor and Jeffrey I. Seeman

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Department of Chemistry
Colorado State University
Fort Collins, Colorado 80523

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ABSTRACT

The sterically hindered styrene derivative, α -methylstyrene (2-phenylpropene), is studied by 1-color time-of-flight mass spectroscopy (TOFMS). In contrast to styrene, which has an intense spectral origin transition in the TOFMS, α -methylstyrene exhibits a weak origin transition. A progression in a low frequency torsional mode, with an energy level spacing of $269/\text{cm}^{-1}$, is built on the origin. The intensity maximum of this progression occurs at the eighth peak position, indicating that the ground and excited state geometries are displaced from one another. The torsional progression is assigned to the hindered rotation of the propenyl group with respect to the aromatic ring. Potential parameters derived from an analysis of the spectra are $V_2 = 0.0$ and $V_4 = 150.0/\text{cm}^{-1}$ for S_0 and $V_2 = 4867$, $V_4 = -500$ and $V_6 = -80/\text{cm}^{-1}$ for S_1 . Based on hot band transitions in the region of the origin, this torsional mode is assigned an energy level spacing of $32/\text{cm}^{-1}$ in the ground state. In the ground state, the propenyl group is calculated to be at a 31° angle from the plane of the aromatic ring. Analysis of the Franck-Condon intensity profile yields a displacement in the excited state, for the angle between the aromatic and ethylenic groups, of 30° relative to the ground state. α -Methylstyrene is suggested to be nearly planar in its first excited $\pi-\pi^*$ state.

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V.H. Grassian and E.R. Bernstein

Colorado State University

Department of Chemistry

Fort Collins, Colorado 80523

and

Henry V. Secor and Jeffrey I. Seeman

Philip Morris Research Center

P.O. Box 26583

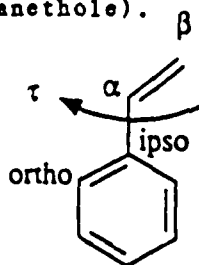
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ABSTRACT

The sterically hindered styrene derivative, α -methylstyrene (2-phenylpropene), is studied by 1-color time-of-flight mass spectroscopy (TOFMS). In contrast to styrene, which has an intense spectral origin transition in the TOFMS, α -methylstyrene exhibits a weak origin transition. A progression in a low frequency torsional mode, with an energy level spacing of $\sim 69 \text{ cm}^{-1}$, is built on the origin. The intensity maximum of this progression occurs at the eighth peak position, indicating that the ground and excited state geometries are displaced from one another. The torsional progression is assigned to the hindered rotation of the propenyl group with respect to the aromatic ring. Potential parameters derived from an analysis of the spectra are $V_2 = 0.0$ and $V_4 = 150.0 \text{ cm}^{-1}$ for S_0 and $V_2 = 4867$, $V_4 = -500$ and $V_6 = -80 \text{ cm}^{-1}$ for S_1 . Based on hot band transitions in the region of the origin, this torsional mode is assigned an energy level spacing of $\sim 32 \text{ cm}^{-1}$ in the ground state. In the ground state, the propenyl group is calculated to be at a $\sim 31^\circ$ angle from the plane of the aromatic ring. Analysis of the Franck-Condon intensity profile yields a displacement in the excited state, for the angle between the aromatic and ethylenic groups, of 30° relative to the ground state. α -Methylstyrene is suggested to be nearly planar in its first excited $\pi-\pi^*$ state.

I. INTRODUCTION

Styrene (1) has been the subject of numerous experimental and theoretical studies, in part because it is the prototypic molecule containing an aromatic ring- sp^2 bond.¹⁻¹³ Styrene is planar in its ground and first excited singlet states and has a low barrier to rotation about its sp^2 - sp^2 bond in S_0 (<4 kcal/mol).^{2,9-13} Recently, using supersonic molecular jet spectroscopy, we have shown that sterically unhindered styrene derivatives also have planar conformations in both S_0 and S_1 .^{12,13} In addition to styrene itself, the molecules examined by this technique included trans- β -methylstyrene, 3-methylstyrene, 4-ethylstyrene, and 4-methoxy-trans- β -methylstyrene (anethole).

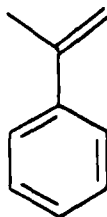


1

$$\tau = \tau(C_{ortho}-C_{ipso}-C_{\alpha}-C_{\beta})$$

Of the vast literature regarding conformational preferences and rotational barriers for molecules containing an sp^2 - sp^2 bond,¹⁴ most studies have been performed (out of experimental necessity¹⁵) on highly substituted molecules. The energy gain from π -conjugation in an extended planar geometry is countered by an energy loss from steric interactions which are maximum in the planar conformation. Consequently, bulky substituents on or near the sp^2 - sp^2 bond not only raise the barrier to rotation about this bond but also modify the conformational profile: the stable planar conformer for styrene becomes the energy maximum for sterically hindered styrenes.^{10,11,14} The present work extends our laser jet studies and focuses attention on α -methylstyrene (2) which contains the smallest stepwise jump in steric

hindrance on the styrene framework ($H \rightarrow CH_3$).



2

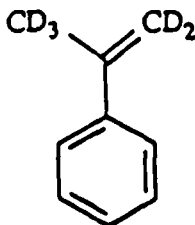
The non-planarity of 2 in the ground state has been postulated from the decrease in λ_{\max} relative to that of styrene for the $\pi-\pi^*$ (S_1-S_0) transition of 2 in solution.⁴ The deviation from planarity (as defined by the angle τ) for 2 has been estimated to be 33° in S_0 based on solution phase absorption data.⁴ Recent molecular mechanics-molecular orbital (MOMM) calculations have suggested that τ for α -methylstyrene is 36° in S_0 . The conformation of this molecule in the excited state has until the present, not been reported.

Supersonic molecular jet spectroscopy is ideally suited for the conformational studies of sterically hindered styrenes. The rotationally and vibrationally cooled molecules produced in the expansion exhibit uncongested spectra relative to room temperature gas phase spectra.¹⁶ If a displacement τ of the energy minimum ($\tau \neq 0$) relative to the ground state, occurs in the excited state, a progression in the spectral features associated with the torsional motion will be observed in the excitation spectrum. The extent of such changes upon excitation can be calculated from a Franck-Condon intensity analysis. This type of torsional progression for non-rigid systems cooled in a supersonic jet expansion has been observed for biphenyl,¹⁷ 9-phenylanthracene,¹⁸ and 9-(2-naphthyl)-anthracene,¹⁹ and torsional analysis has been successfully applied to the spectra thereby obtained.

II. EXPERIMENTAL

The supersonic jet expansion as well as the time-of-flight mass spectrometer have been described previously.²⁰ Briefly, the supersonic expansion is generated using a pulsed R.M. Jordan valve. Helium is used as the carrier gas at a pressure of 3 to 4 atm. Argon is used for the carrier gas in determining the spectroscopic origin so as to eliminate any hot bands in that region. A tunable pulsed dye laser, which is pumped by the second harmonic (532 nm) of a Nd:YAG laser, is frequency doubled and focused with a 1 meter quartz lens into the vacuum chamber. Fluorescein dye is used in all of these experiments. The ions are produced by sequential photon absorption and are accelerated into the flight tube where they are detected by a microchannel plate.

α -Methylstyrene was purchased from Aldrich and used without further purification. All compounds are stored in the dark at 4°C to prevent polymerization. α -Methyl- d_3 -styrene- β,β - d_2 (3) was prepared by deuterium exchange of the methyl hydrogens of acetophenone. The resulting methyl- d_3 -phenylketone was allowed to react with methyl- d_3 -magnesium bromide (Grignard reaction) to give dimethyl- d_6 -phenylmethanol which was in turn dehydrated with DCl to yield 3. Full details are described in the supplementary section.



3

III. RESULTS

The time-of-flight mass spectrum of 2 is shown in Figure 1. The

spectrum extends from the origin, 0_0^0 transition, to 1500 cm^{-1} higher in energy. A progression in a low frequency mode built on the origin is clearly visible in the spectrum. The spacing of this progression is $\sim 69\text{ cm}^{-1}$. Table I lists the frequencies of the progression as well as the spacings between each energy level. The spacings between the energy levels become larger at higher levels. This negative anharmonicity suggests that the potential energy surface, for this motion in the excited state, is flat near the equilibrium angle but has steeply rising walls.²¹ This low frequency motion is also built on other spectral features, i.e. higher vibrational modes.

The origin region is shown in an expanded scale in Figure 2. Both argon and helium were each used as the carrier gases in determining the position of the spectral origin so as to eliminate any hot bands in the spectrum. The lowest frequency peak at 35063.7 cm^{-1} is assigned to the spectral origin, i.e. the 0_0^0 transition.

The TOFMS of 3 is shown in Figure 3, recorded from 35000 to 36000 cm^{-1} . Listed in Table II are the energies of the low frequency vibration and the energy level spacings for its progression for the partially deuterated compound. The frequency of this mode is reduced to $\sim 64\text{ cm}^{-1}$ upon deuteration of the propenyl group. The most intense feature in the progression occurs at the seventh peak position. The 0_0^0 transition is determined to be at 35083.6 cm^{-1} .

Although the spectra of 2 and 3 are quite congested, the other higher frequency vibrational modes of α -methylstyrene in the excited state can be determined. One mode is observed at a frequency of 369.5 cm^{-1} which shifts to 341.1 cm^{-1} in the partially deuterated compound (compare Figures 1 and 3).

The other peak identified as a vibrational mode occurs at 738.7 cm^{-1} for 2 and 722.1 cm^{-1} for 3. The frequencies of these vibrations are listed in Table II. The low frequency progression is built on both of these vibrations, with an energy level spacing of approximately 69 cm^{-1} for 2 in the excited state. The progression built on these two vibronic features are similar in intensity to that observed for the origin; the maximum peak intensity for the progression occurs at the ninth member.

Information on this 69 cm^{-1} mode can be obtained for the ground state as well. At low backing pressures for the expansion ($<40\text{ psig He}$), hot bands appear around the origin. Figure 4 shows such spectra from which the torsional mode energy in the ground state can be determined to be ca. 32 cm^{-1} . Clearly, however, the ground state value of this mode cannot be as well determined as the excited state value of this mode.

IV. ANALYSIS AND DISCUSSION

A. Assignment of the Low Frequency Mode

Assignment of the low frequency mode, identified as $\sim 69\text{ cm}^{-1}$ in S_1 and $\sim 32\text{ cm}^{-1}$ in S_0 of α -methylstyrene (2), can be made based on the following two considerations. First, a comparison of the origin region of 2 ($0_0^0 + 200\text{ cm}^{-1}$) with that of styrene (1) (Figure 5). In contrast to the spectrum of (2) (Figure 1), the 0_0^0 transition of styrene is intense and the origin region is devoid of any spectral features up to 200 cm^{-1} . Second, the mode undergoes a substantial shift (from 69 to 64 cm^{-1}) upon deuteration of the propenyl group. We conclude, therefore that this low frequency mode can be assigned to the torsional motion whose displacement is indicated by τ in 2.

The repulsive steric interactions between the α -methyl group, the syn

β -vinyl hydrogen and the ortho hydrogens destabilize the planarity of 2. The potential energy surface for this molecule has a minimum at some angle τ not equal to zero, i.e., the planar conformation is unfavorable for this sterically hindered styrene derivative in one or both of the electronic states S_0 and S_1 . The potential energy surface for styrene and its derivatives reflects the stabilizing effects of conjugation and the destabilizing effects of steric repulsive interactions.

A displacement along the coordinate τ occurs in the excited state, with respect to the ground state, as is evidenced by the presence of Frank-Condon intensity envelope of this motion in the jet-cooled excitation spectrum (measured using the TOFMS technique). The change in the torsion angle τ can be determined from a Franck-Condon intensity analysis of the spectrum. Since such an analysis depends on accurate torsional eigenvectors for both the ground and excited states, prior to a Franck-Condon calculation the form of the potential surface must be determined for the molecule. The form of the potential and the eigenvalues and eigenvectors for the torsional motion are discussed in Section IV-C below.

B. Assignment of Higher Frequency Vibrational Modes

Vibrational assignments for two of the higher energy modes of 2 in S_1 can be made from a comparison of the present results with those for styrene³ (see Table III). The $6a^1$ vibration at 394.5 cm^{-1} in styrene shifts to lower energy for both 2 and 3, 369.5 cm^{-1} and 341.1 cm^{-1} respectively. The 1^1 vibration in the excited state of 2 is assigned to the peak at 738.7 cm^{-1} shifted to 722.1 cm^{-1} for the partially deuterated compound. These energies can be compared to the energy of the 1^1 vibrational mode for styrene which is at 745.8 cm^{-1} .

C. Calculations of the Torsional Energy Levels and Franck-Condon Factors

A one-dimensional rotor analysis is used to fit the frequencies of the torsional mode. The general form of the potential function can be expressed as a cosine Fourier series,

$$V(\tau) = \frac{1}{2} \sum_n V_n (1 - \cos n \tau). \quad (1)$$

The Hamiltonian of the free rotor is then modified by including this potential term. The Schroedinger equation for the hindered rotor can be written as:

$$\left[-B \frac{\partial^2}{\partial \tau^2} + V_n(\tau) \right] \psi_m(\tau) = E_m \psi_m(\tau), \quad (2)$$

in which B is the reduced rotational constant for the internal torsional mode. Free rotor wavefunctions are used as a basis set in the diagonalization of the Hamiltonian in eq (2): a total of 109 basis functions are needed to ensure convergence of all the energy levels. The best fit to the excited state data for 2 and 3 using eq (2) is obtained with the following parameters: $V_2 = 4867.0$, $V_4 = -500.0$, $V_6 = -80.0 \text{ cm}^{-1}$ and $B = 0.444 \text{ cm}^{-1}$ for 2 and $B = 0.387 \text{ cm}^{-1}$ for 3. The inclusion of a V_6 term is necessary to reproduce the large negative anharmonicity in the energy level spacings (see Tables I and II). Table IV lists the observed and calculated energy level values, the two are in good agreement for both 2 and 3.

The form of the ground state potential should differ somewhat from that of the excited state. We assume that the ground state potential should have maxima at $\tau=0$ and $\tau=90$ degrees. The reason for the potential being a maximum at $\tau=0^\circ$ has been discussed above and is attributed to the steric interaction between the propenyl substituent and the ortho-hydrogens. The complete loss of resonance stabilization between the aromatic and ethylenic π -systems at $\tau=90^\circ$ causes the potential to be a maximum at this angle also.

The dominant term in the potential function will then be a V_4 term with maxima at 0, 90, 180 and 270 degrees.

Employing a potential for the ground state torsional motion with a dominant V_4 term and a small V_2 term, we find $V_2 = 0.0 \text{ cm}^{-1}$ and $V_4 = 150.0 \text{ cm}^{-1}$ ($B = 0.444 \text{ cm}^{-1}$) for the best fit to the ca. 32 cm^{-1} observed ground state torsional mode.

The displacement in the coordinate in the excited state with respect to its ground state equilibrium position can be determined by a Franck-Condon intensity analysis of the torsional progression. The eigenvectors for the torsional motion can be written as $\Psi_e(\tau)$ and $\Psi_g(\tau+\Delta\tau)$ for the ground and excited states, respectively. The Franck Condon factors for transitions from the lowest level in the ground state potential well (zero point level) to the torsional levels of the excited state potential surface can be written as:

$$\langle \Psi_e(\tau+\Delta\tau) | \Psi_g(\tau) \rangle \quad (3)$$

$$= \langle \sum_m^e c_m^e \phi_m(\tau+\Delta\tau) | \sum_m^g c_m^g \phi_m(\tau) \rangle \quad (4)$$

$$= \langle \sum_m^e c_m^e c_m^g \langle \phi_m(\tau+\Delta\tau) | \phi_m(\tau) \rangle \rangle \quad (5)$$

$$= \langle \sum_m^e c_m^e c_m^g \cos m(\Delta\tau) \rangle \quad (6)$$

$$m = 0, \pm 1, \pm 2, \pm 3 \dots$$

These Franck-Condon calculations give a displacement angle in τ of $30 \pm 5^\circ$ for an intensity pattern in which the eighth peak position is a maximum. The uncertainty in the displacement angle is caused by two factors: the approximate form of the ground state potential and the uncertainty in the maximum intensity peak position (8 ± 1).

D. Determination of the Equilibrium Value of τ in the Ground and Excited States

The analysis presented above demonstrates that the equilibrium torsional angle τ is not the same in the ground state and excited states of 2 and 3: only the displacement of τ , $\Delta\tau$, between the two states is known. The relationship between the geometry of molecules and their electronic absorption spectra has been discussed by Suzuki.⁵ We follow the method developed and employed by Suzuki, which employs orbital theory to determine the ground state geometry of 2 in solution, and apply it to the supersonic jet data of 2.

The resonance energy associated with the interaction between the aromatic and ethylenic π systems of styrene is at a maximum at $\tau = 0^\circ$ and a minimum at $\tau = 90^\circ$. The energy of the electronic transition increases as τ increases from 0 to 90° . In the limit of $\tau = 90^\circ$, the two π systems are orthogonal to each other and the electronic absorption spectrum, in particular the 0_0^0 transition energy, should be similar to that of an alkylbenzene. In the limit of maximum resonance energy ($\tau = 0^\circ$), the electronic transition energy will be similar to that found for sterically unhindered substituted styrenes, such as trans- β -methylstyrene which is known to be planar.¹²

These transition energies have been calculated,⁵ using Huckel theory for the planar and perpendicular limits. The analysis considers only a one electron transition and neglects relaxation effects. The calculated and the experimentally determined transition energy are assumed to be linearly related in this treatment. The transition energy for $0^\circ < \tau < 90^\circ$ can be calculated from the equation,

$$\Delta E = \Delta E_{\tau=90} - \frac{(\Delta E_{\tau=90} - \Delta E_{\tau=0}) (\nu_{\tau=90} - \nu)}{(\nu_{\tau=90} - \nu_{\tau=0})} . \quad (7)$$

$\Delta E_{\tau=90}$ and $\Delta E_{\tau=0}$ are taken from the calculations of Suzuki and are equal to 1.4744 and 2, in units of $-\beta$, respectively. The reference values of the experimentally determined energies $\nu_{\tau=90}$ and $\nu_{\tau=0}$ are taken as the 0_0^0 transition energies of isopropylbenzene and trans- β -methylstyrene which are 37668.5 and 34585.0 cm^{-1} , respectively. Using these values, $\Delta E(-\beta)$ is calculated to be 1.5556. Figure 6 shows the angle τ plotted as a function of ΔE (taken from the tabulated values given by Suzuki): the value $\tau = 31^\circ$ correlates with the calculated value of ΔE . The gas phase value calculated here is almost identical to the calculated value of τ for 2 in solution ($\tau=33^\circ$).⁴

The excited state torsion angles for 2 can then be one of two values, ~ 0 or $\sim 60^\circ$. In analogy to biphenyl,^{17,21} we suggest the first excited state of 2 to be nearly planar (i.e., $\tau \sim 0^\circ$).

V. CONCLUSIONS

The TOFMS of α -methylstyrene has been presented and analyzed. The ground state torsional angle τ is calculated to be $\sim 31^\circ$. A Franck-Condon analysis yields a displacement $\Delta\tau$ in the excited state of 30° : we suggest this implies a nearly planar conformation for 2 in its first excited state S_1 . The potential parameters determined from a hindered rotor analysis of the internal torsional motion of 2 yields ground state parameters $V_2 = 0.0$ and $V_4 = 150.0 \text{ cm}^{-1}$ and excited state parameters of $V_2 = 4867$, $V_4 = -500$ and $V_6 = -80 \text{ cm}^{-1}$ with a reduced rotational constant of $B = 0.444 \text{ cm}^{-1}$.

Acknowledgment:

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15. In the absence of severe steric hindrance, the activation energy for rotation about an sp^2-sp^2 bond is only a few kcal/mol: too low to be detected by dynamic NMR spectroscopy.¹⁴ For systems which are not coplanar about the sp^2-sp^2 bond, rotation corresponds to racemization of the molecule and suitable substituents on or near the sp^2-sp^2 bond can then serve as experimental monitors' of the rotational processes.^{14a}
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TABLE I
 α -Methylstyrene torsional structure
about the origin transition (35,063.7 cm⁻¹).

	Energy (cm ⁻¹)	Spacing (cm ⁻¹)
T_0^0	0.0	
T_0^1	63.6	63.6
T_0^2	127.6	64.0
T_0^3	194.0	66.4
T_0^4	262.0	68.0
T_0^5	330.0	68.0
T_0^6	401.6	71.6
T_0^7	472.1	70.5
T_0^8	543.2	71.1
T_0^9	614.6	71.4
T_0^{10}	687.7	73.1
T_0^{11}	760.0	72.3

TABLE II

α -Methyl- d_3 -styrene- β,β - d_2 torsional structure
about the origin transition (35083.6 cm^{-1}).

	Energy (cm^{-1})	Spacing (cm^{-1})
T^0	0.0	
T^1	58.4	58.4
T^2	119.0	60.6
T^3	181.4	62.4
T^4	245.0	63.6
T^5	308.2	63.6
T^6	373.3	65.1
T^7	438.3	65.0
T^8	504.3	66.0
T^9	570.8	66.5
T^{10}	639.3	68.5

TABLE III
Vibrational Mode Assignments

Assignment	Frequencies (cm ⁻¹)		
	α -methylstyrene	α -methyl-d ₃ -styrene- β,β -d ₂	styrene*
1 ⁰	738.7	722.1	745.8
6a ¹	394.5	341.1	369.5

* The vibrational energies for jet-cooled styrene are taken from reference 3.

TABLE IV

Calculated and Observed Energies (cm^{-1}) of the Torsional Motion of
 α -Methylstyrene and α -Methylstyrene- d_5 in S_1 .

	α -methylstyrene		α -methyl- d_3 -styrene- $\beta,\beta\text{-d}_2$	
	observed	calculated ^a	observed	calculated ^b
T^0	0.0	0.0	0.0	0.0
T^1	63.6	63.5	58.4	59.2
T^2	127.6	128.6	119.0	119.8
T^3	194.0	195.0	181.4	181.6
T^4	262.0	262.7	245.0	244.5
T^5	330.0	331.5	308.2	308.3
T^6	401.6	401.1	373.3	373.1
T^7	472.1	471.6	438.3	438.5
T^8	543.2	542.9	504.3	504.7
T^9	614.6	614.8	570.8	571.4
T_0	687.7	687.2	639.3	638.8
T_0	760.0	750.2		

^a Potential parameters: $V_2=4867$, $V_4=-500$, $V_6=-80$ and $B=0.444 \text{ cm}^{-1}$

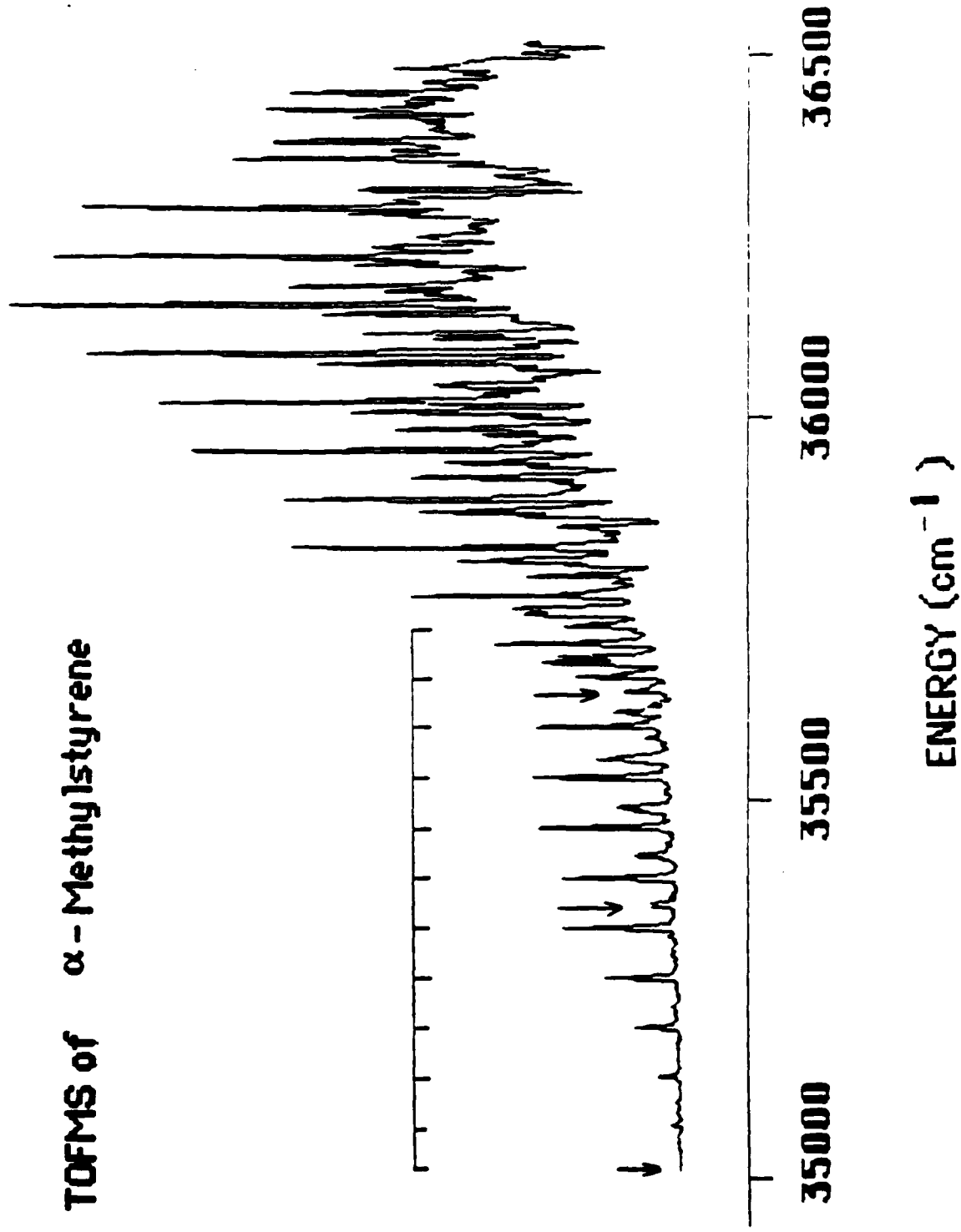
^b Potential parameters: $V_2=4867$, $V_4=-500$, $V_6=-80$ and $B=0.387 \text{ cm}^{-1}$

FIGURE CAPTIONS

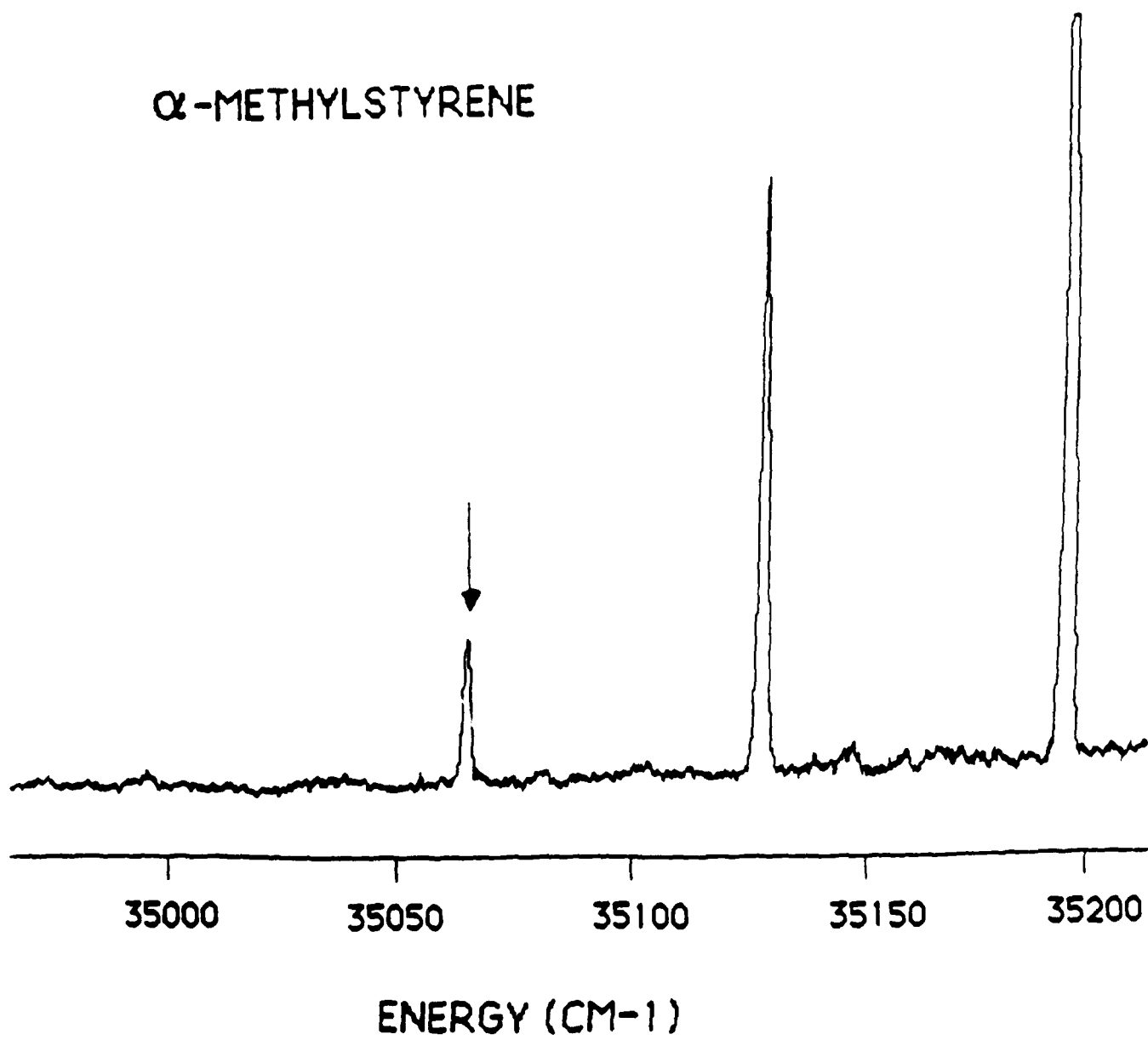
- Figure 1 The TOFMS of α -methylstyrene (2) from ~ 35000 to ~ 36500 cm^{-1} . The origin is very weak in intensity and marked by an arrow. Two other higher vibrational features are also marked by an arrow in the spectrum. A low frequency motion which is built on the origin and higher vibrations is seen in the spectrum with an energy level spacing of 69 cm^{-1} .
- Figure 2 An expanded view of the origin transition region of 2 (see fig. 1). The 0_0^0 transition is identified at 35063.7 cm^{-1} .
- Figure 3 The TOFMS of α -methyl- d_3 -styrene- $\beta,\beta\text{-d}_2$ (3) scanned from 35000 to 36000 cm^{-1} . The origin are marked by arrows and two higher vibrational features. A low frequency mode is seen in the spectrum which has a spacing of ~ 64 cm^{-1} .
- Figure 4 TOFMS of α -methylstyrene at low He expansion pressures. Hot band transitions are observed for the torsional motion of the propenyl group.
- Figure 5 The one-color TOFMS of styrene (1). The origin region consists solely of an intense peak with no other spectral features up to 200 cm^{-1} . The 0_0^0 transition is at 34778.7 cm^{-1} from reference 12. Reprinted with permission from the American Chemical Society.

Figure 6 The electronic transition energy plotted as a function of the torsional angle τ for styrene and its derivatives, as calculated by Suzuki (see reference 5).

TOFMS of α -Methylstyrene

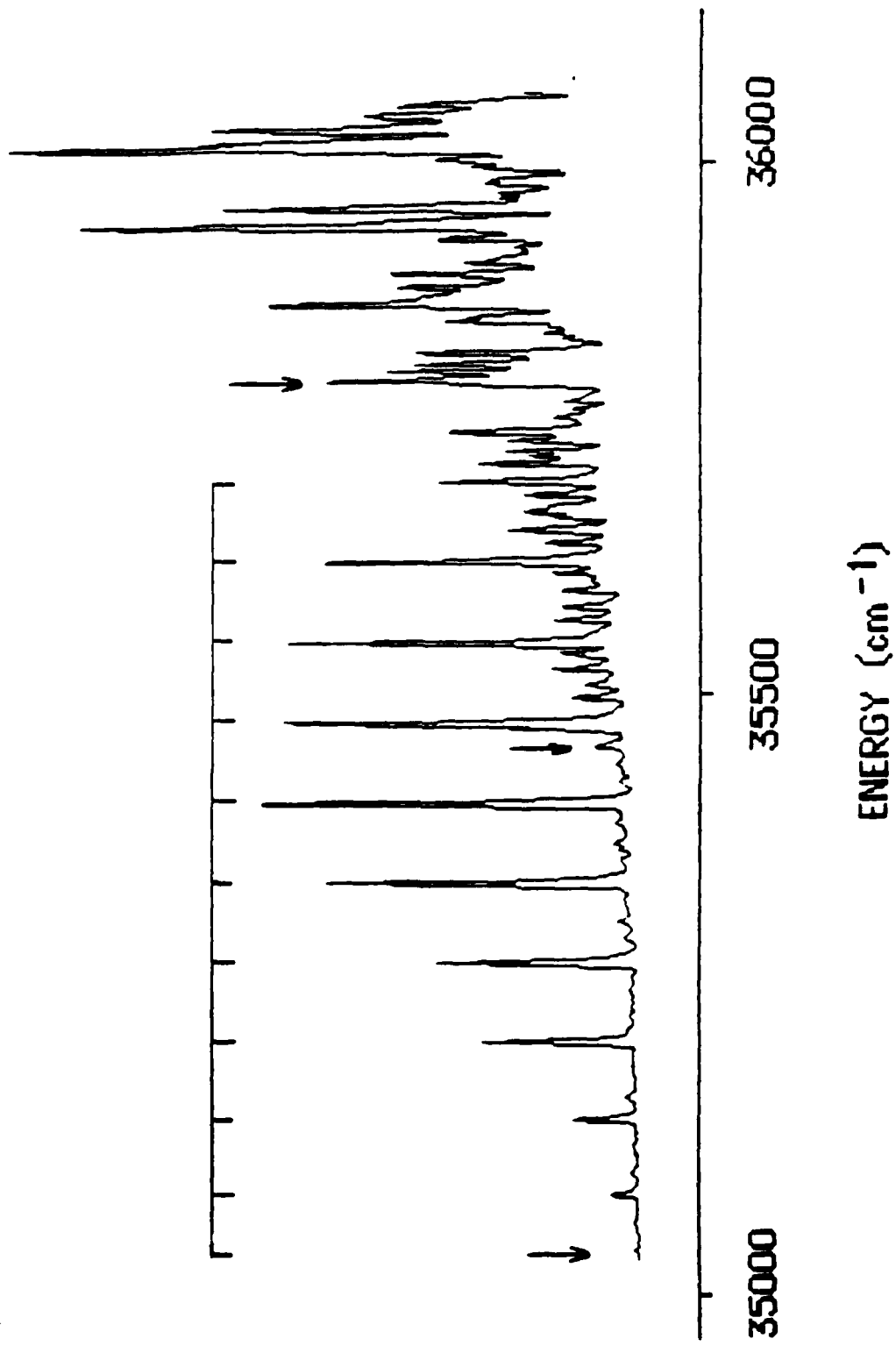


α -METHYLSTYRENE

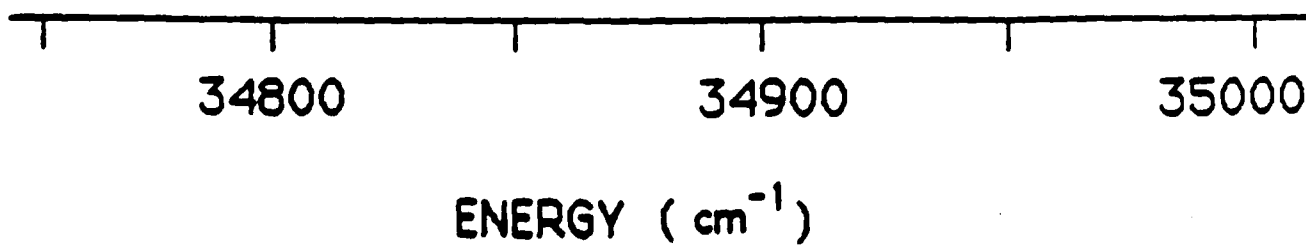
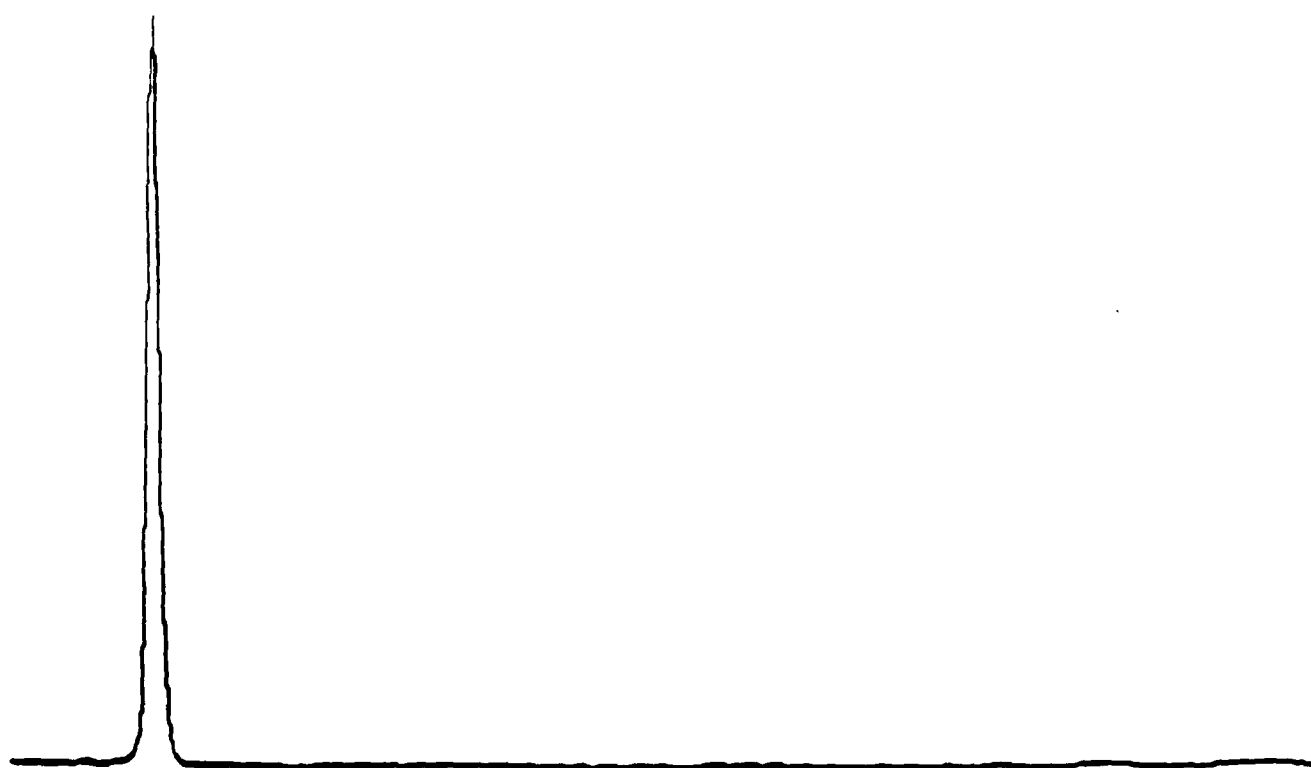


2

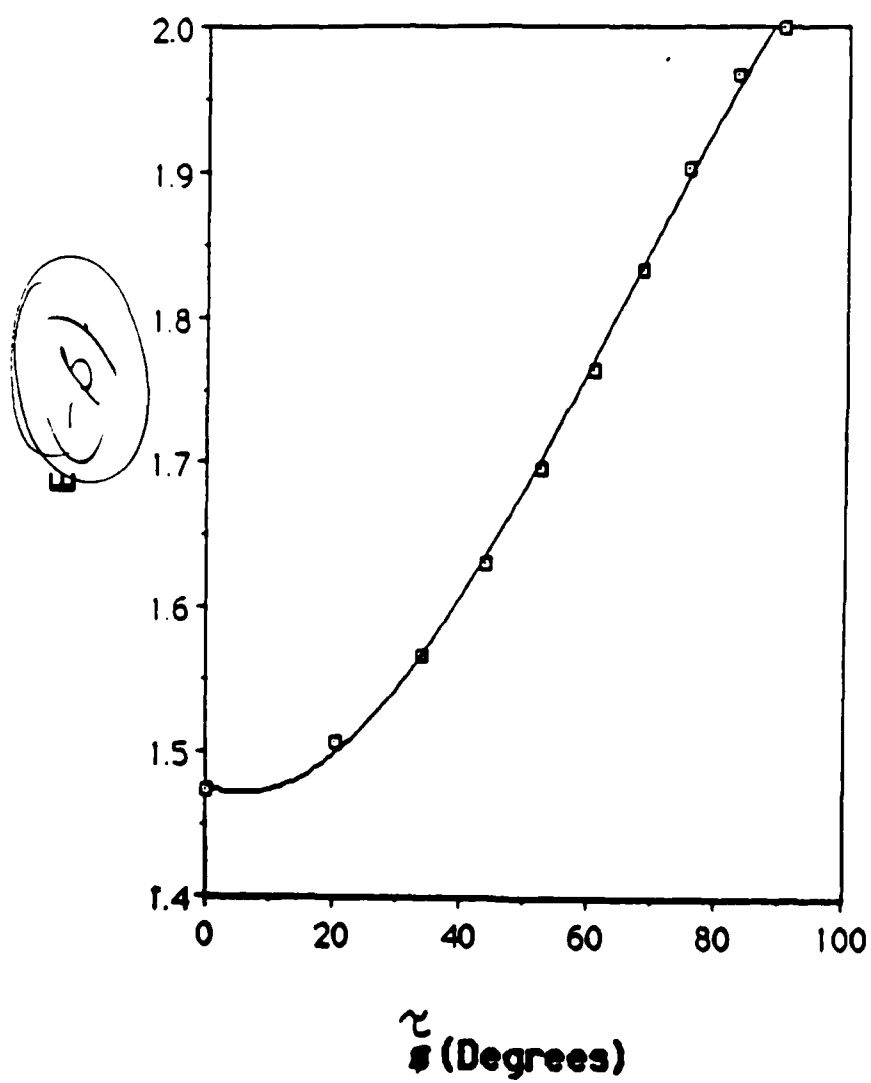
TOFMS of d₅- α -Methylstyrene



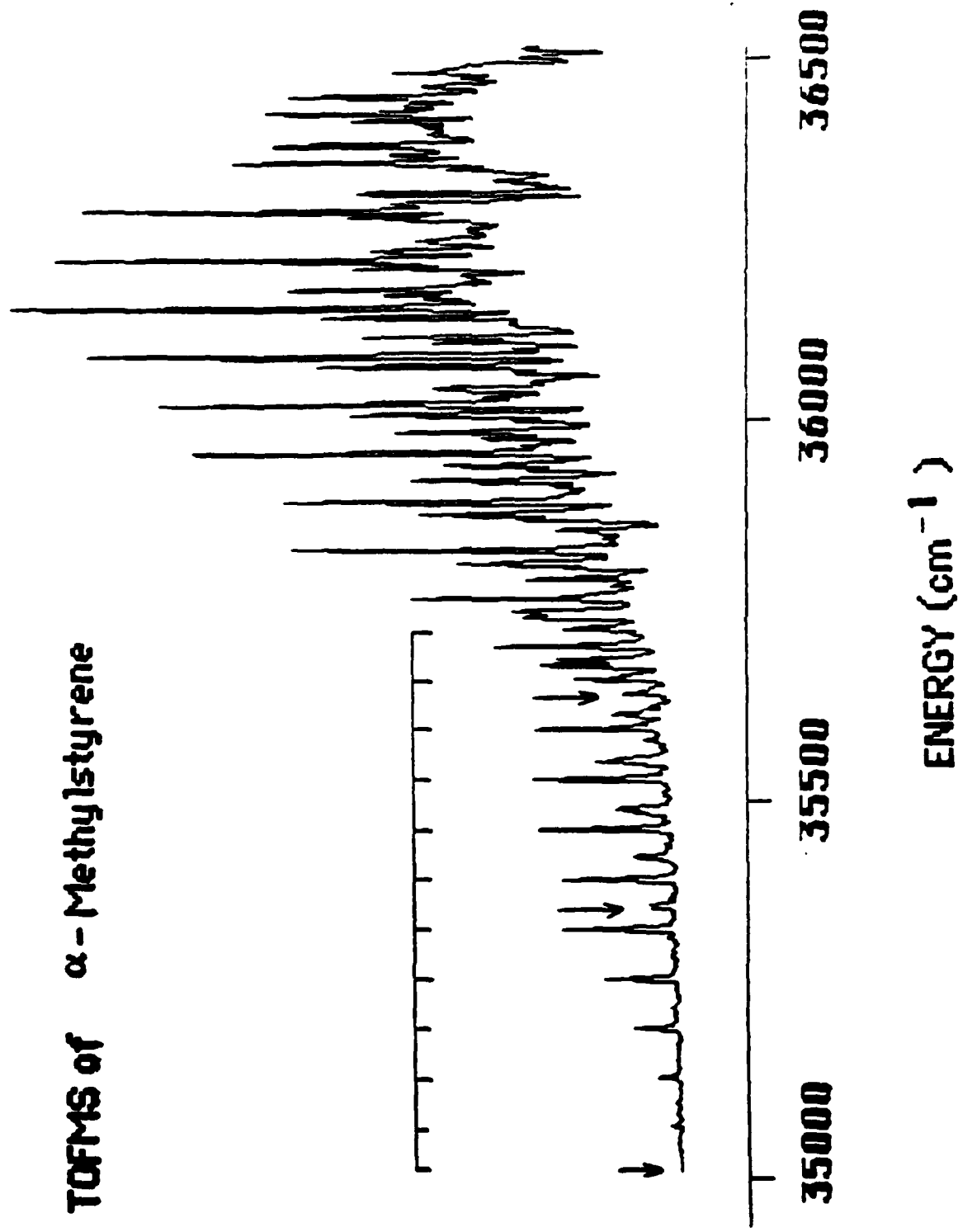
TOFMS of Styrene



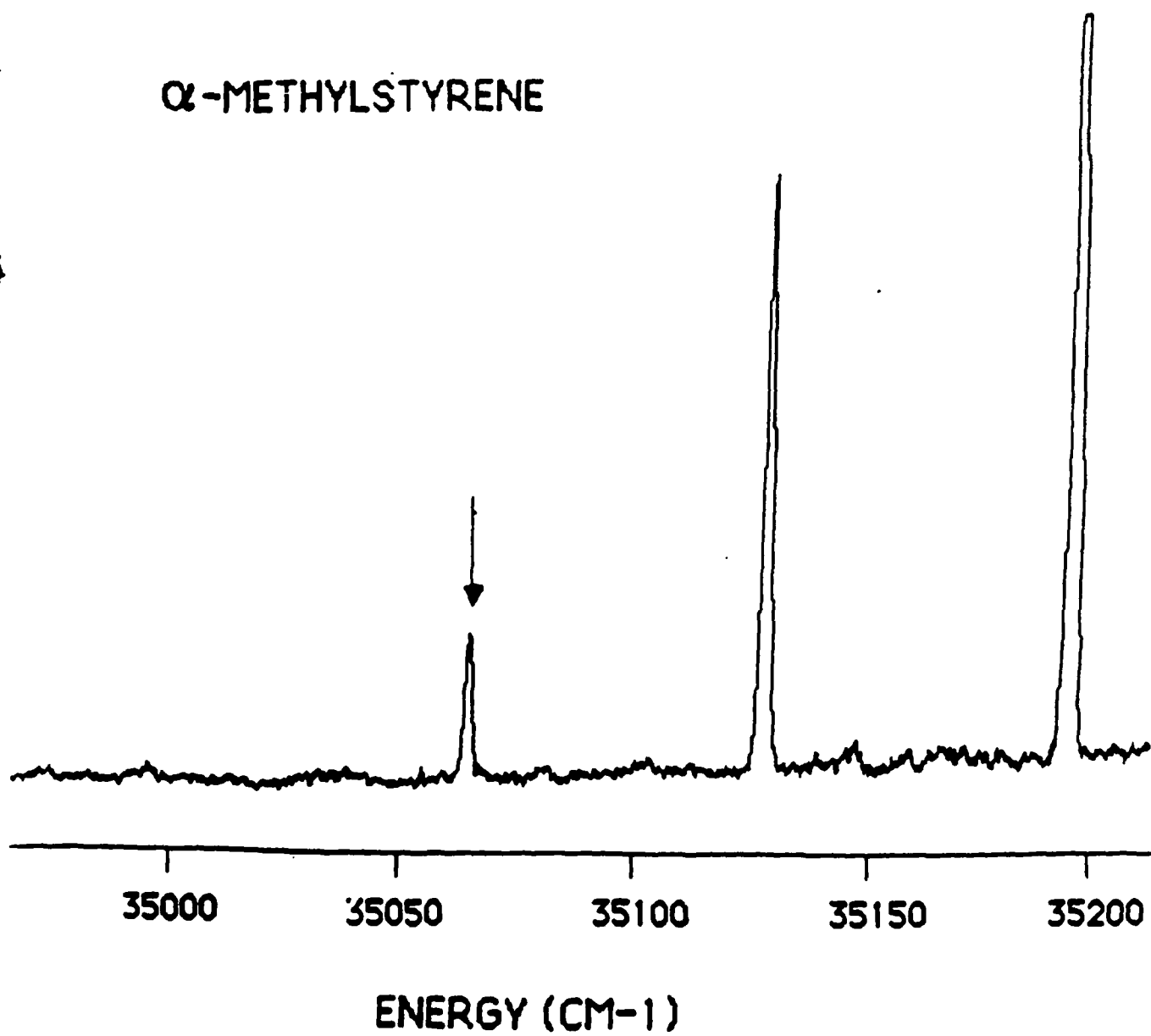
5



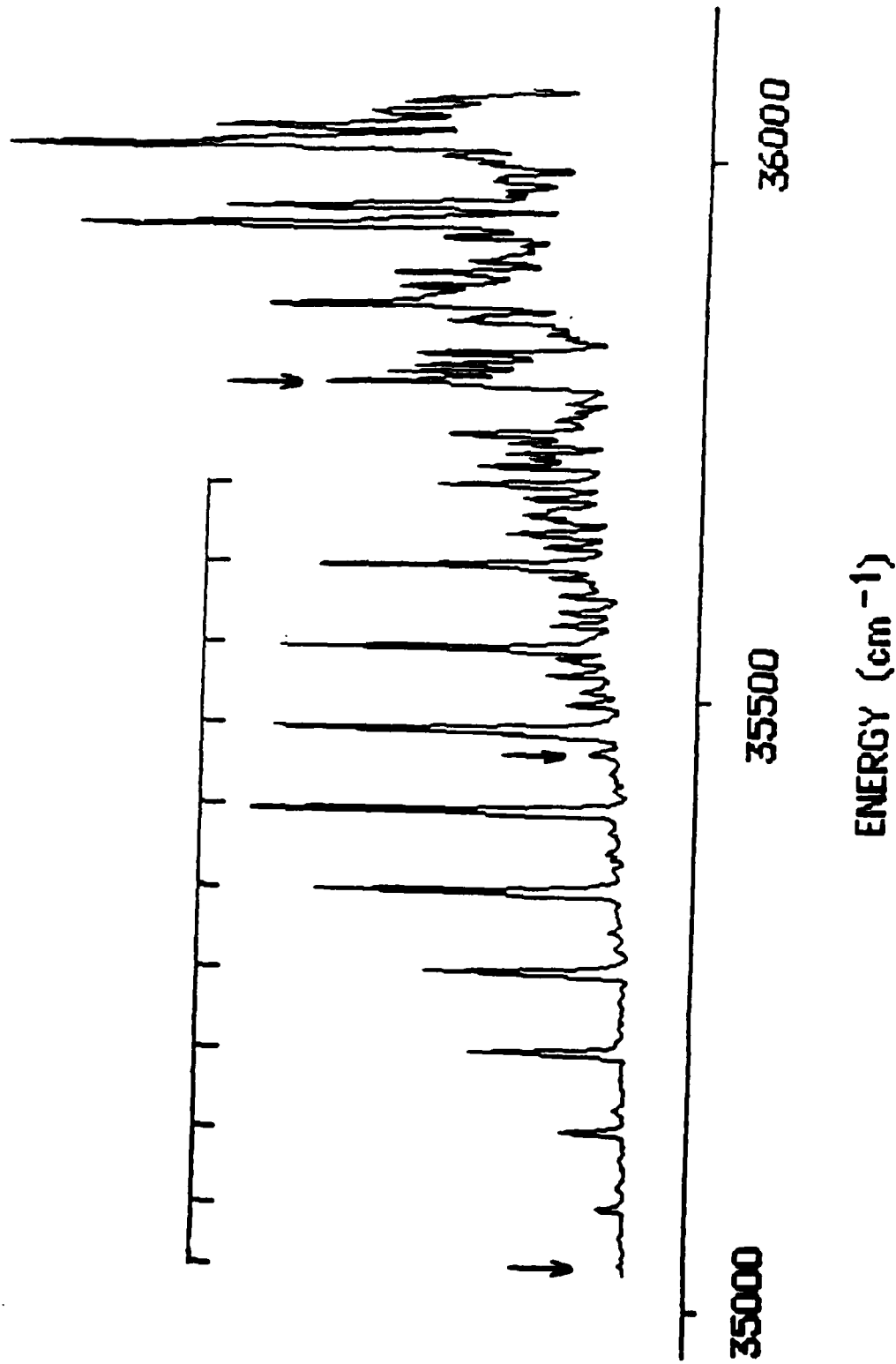
TOFMS of α -Methylstyrene



α -METHYLSTYRENE



TOFMS of d₅- α -Methylstyrene



-Methylstyrene

($P_{He} < 40$ psig)



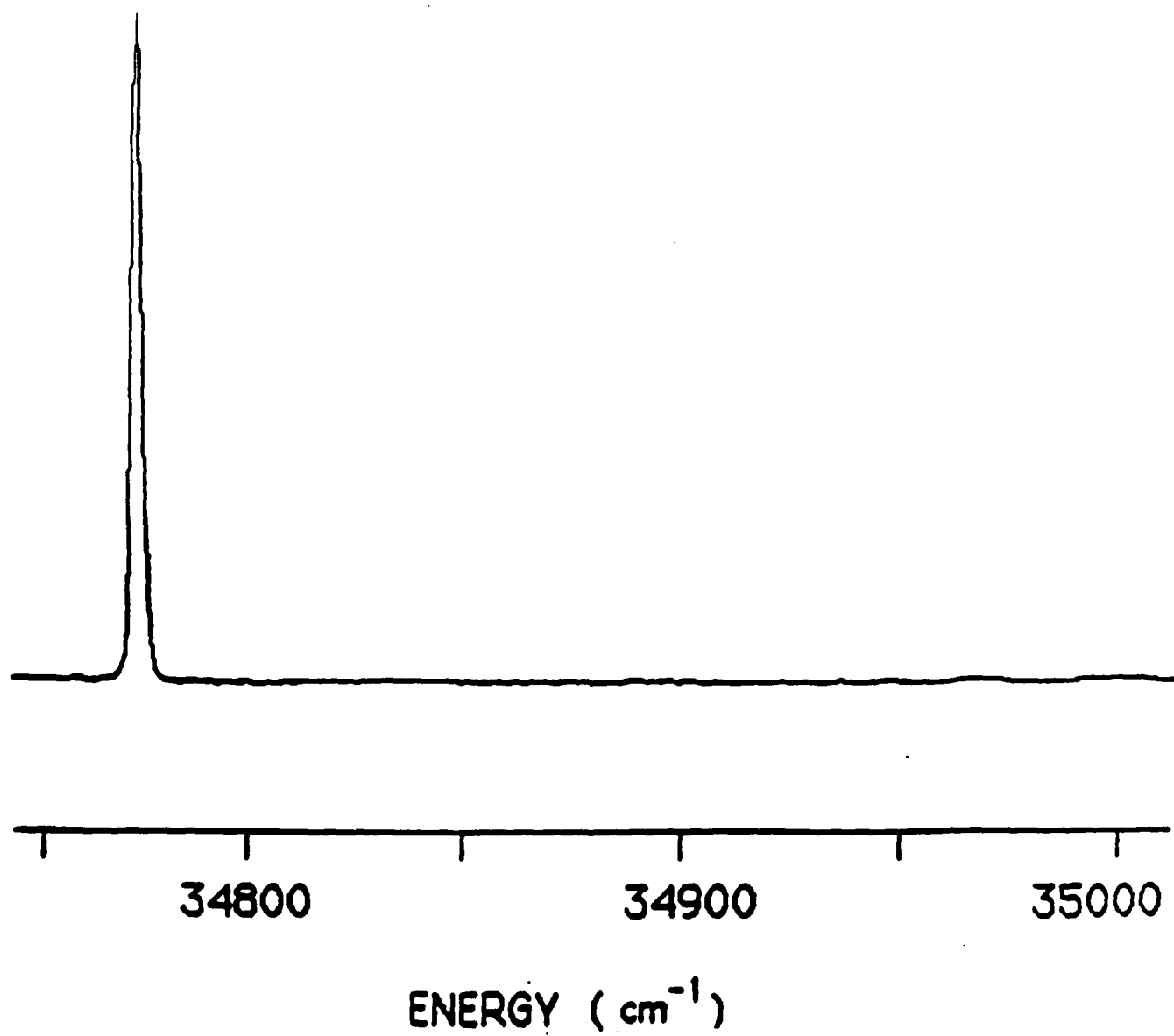
34800

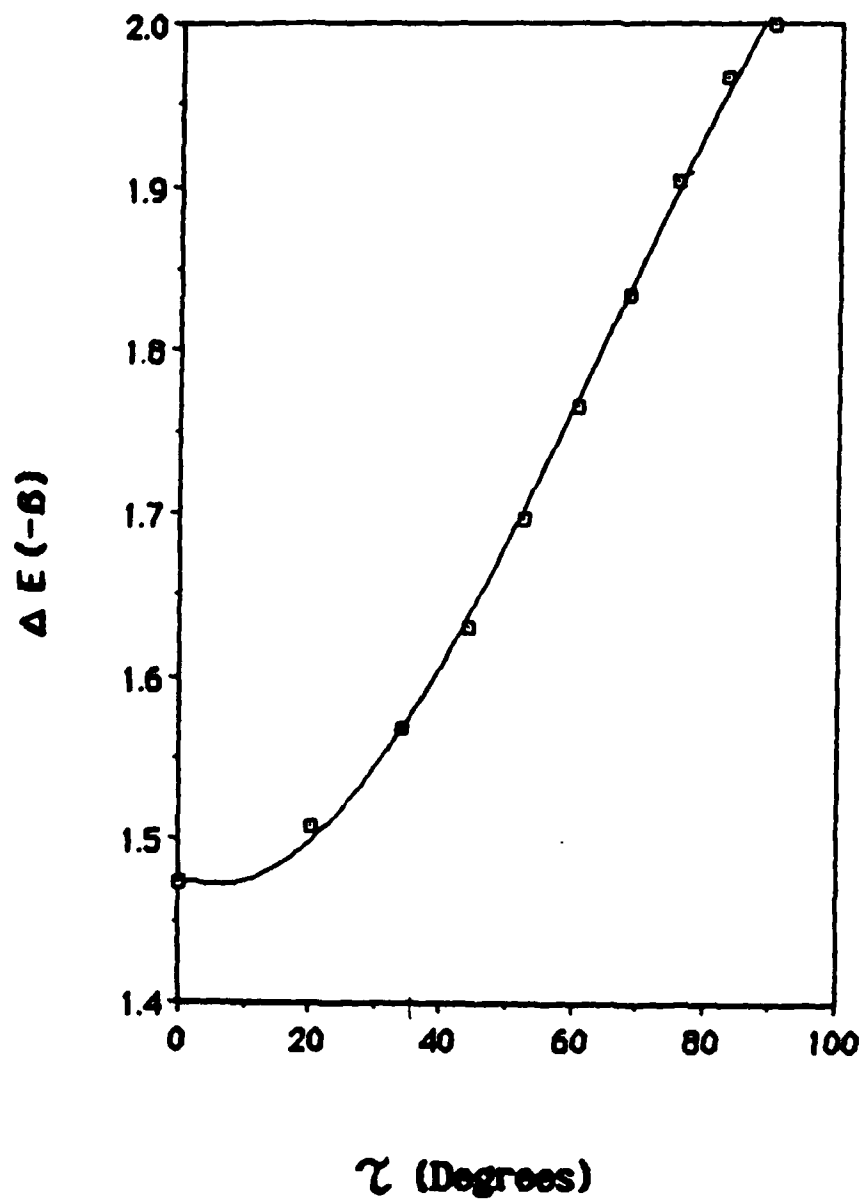
34900

35000

ENERGY (cm^{-1})

TOFMS of Styrene





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